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LITHIUM SECONDARY BATTERY  
[Lichiumu niji denchi]

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[Claims]

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[Claim 1] A lithium secondary battery having a porous separator between the anode and cathode, arranging a lithium oxide on the anode, filling with non-aqueous electrolytes, and the cathode material arranged on the cathode has a composition expressed by  $M_{100-x}Si_x$  ( $x \geq 50$  at%), and M being at least one element selected from Ni, Fe, Co, and Mn.

[Claim 2] A lithium secondary battery according to Claim 1, wherein  $55 < x < 85$ at% for the cathode material.

[Claim 3] A lithium secondary battery having a porous separator between the anode and cathode, arranging a lithium oxide on the anode, filling with non-aqueous electrolytes, and the cathode material arranged on the cathode has a composition expressed by  $M_{100-x-y}B_ySi_x$  ( $x \geq 50$  at%,  $0 < y < 10$ at%), and M is at least one element selected from Ni, Fe, Co, and Mn, and in addition, B is at least one element selected from Sn, V, Cu, Ag, and Al.

[Claim 4] A lithium secondary battery according to Claim 3, wherein the cathode material contains at least 3-8at% Sn or V.

[Claim 5] A lithium secondary battery according to any one of the claims from Claim 1-Claim 4 wherein the entire cathode material is crystalline or amorphous in one part.

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\* Paragraph numbers take place for the original pagination in the foreign text.

[Claim 6] A lithium secondary battery according to Claim 5, wherein the cathode crystalline material contains dendrite Si crystals.

[Claim 7] A lithium secondary battery, according to any one of the claims from Claims 4-6 wherein one part of B is deposited on the cathode.

[Detailed Description of the Invention]

[0001] [Field of the Invention]

This invention is related to lithium secondary batteries, especially to optimum cathodes for high capacity.

[0002] [Prior Art]

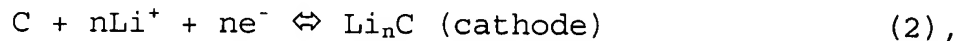
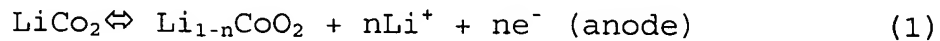
Following the rapid advances in semiconductor technology, recent electronic equipment have made advances in small form, light weight, and multifunctions especially personal computers telephones, AV equipment and the like, and, at the same time, there have been large-scale improvements in convenience. Furthermore, the requirements have intensified for high energy density, long life, and light weight in the secondary batteries used. Conventionally, nickel-cadmium batteries are principally used for small secondary consumer batteries, and in the 1990s, nickel-hydrogen batteries were commercialized on a large scale, and furthermore, there was an impressive technological revolution with the introduction of lithium secondary batteries to the secondary battery marketplace.

[0003] Moreover, considering the characteristics of lithium batteries, their energy density was large compared to conventional batteries, with little self-discharge. The batteries have a wide operable temperature range of -20 to +45 °C. There was no memory effect. They were equivalent. Because of this kind of advantage, conditions in the secondary battery marketplace were principally one of commerce in nickel-cadmium or nickel-hydrogen batteries, but in the near future, it is expected the lithium secondary batteries will replace conventional batteries.

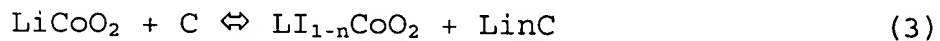
[0004] Lithium cobalt dioxide ( $\text{LiCoO}_2$ ), having high discharge potential can be used along with carbon on the cathode. Electrode material in powder form coats the collector having mixed with the conductor binder to form an electrode. Aluminum foil is used for the anode collector and copper foil for the cathode collector. A porous film such as polyethylene is used on the separator insulating the anode and cathode within the battery. An actual battery stores the anode, separator, and cathode in a cylinder, winding to a roll shape, superimposing the anode, separator, and cathode. Furthermore, organic electrolytes of a non-aqueous system which has melted the support electrolytes (for example,  $\text{LiClO}_4$ ,  $\text{LiPF}_6$ ,  $\text{LiBF}_4$ ) fill the cylinder's interior.

[0005] A lithium secondary battery formed in this way has one part of the lithium within the anode material  $\text{LiCoO}_2$  discharge as ions within the organic electrolytes, and in keeping with this discharge,

the lithium ions of the support electrolytes ( $\text{LiClO}_4$ ,  $\text{LiPF}_6$ ,  $\text{LiBF}_4$ ) which have dissolved in the organic electrolytes, by being stored within the carbon layers of the cathode material, participate in the charging operation. On the other hand, when discharging, the lithium ions which are stored at the cathode are discharged, and the electrons generated flow to external circuits, releasing electrical energy. This is indicated by the following equations for the previously described reactions. The directions of the arrows in the equations indicate a right direction when charging and the reverse direction or left direction when discharging, showing the progress of the chemical reaction.



so that the reaction formula when charging/discharging the entire battery which has combined the anode and cathode is



[0006] When explaining the chemical reaction processes of formulas (1)-(3) from the movement of lithium ions, the following holds. That is, when charging, the lithium in the anode's  $\text{LiCoO}_2$  becomes ions moving within the electrolyte, and the lithium ions within the electrolyte is stored in the cathode's carbon, accumulating as lithium ions. When discharging, the reverse reaction occurs, and the lithium ions within the carbon of the cathode material move within the electrolyte, and the lithium ions within the

electrolyte, being stored within the anode material becomes  $\text{LiCoO}_2$ . In this way, because the active material of the anode and cathode discharge the lithium ions or store, discharge, and charge, it is necessary to provide materials which give efficient chemical reactions for the materials which are used for the anode and cathode.

[0007] [Problems that the Invention is to Solve]

Currently, carbon electrodes are most widely used for the cathodes of lithium secondary batteries. If using carbon for cathodes, having rapidly charged and discharged, the lithium ions within the electrolyte dendritically separate as metal lithium up to the carbon surface, and there is concern that a reduction in capacity will result from the generation of internal short-circuits. In addition, because the energy capacity of the lithium battery compared to other secondary batteries is high, it is especially necessary to restrain from using unstable materials that might be flammable. Because of this concern, materials are obtained as substitutes for flammable carbon. Furthermore, as the higher the density the higher the advantage for discharge capacity per body area, and because carbon has several times lower the density at 2.2g/ml as compared with metal materials, it is difficult to obtain high discharge capacity.

[0008] On the other hand, because carbon as a cathode material contains lithium ions between the crystal layers when charging, the charging capacity is influenced by the lithium storage amount, and carbon use presents a constraint. When there is maximum storage of

lithium in a carbon system cathode, the cathode becomes  $\text{LiC}_6$ . The capacity at this time per unit weight is a comparatively large 370mAh/g, the density per volume is restricted to the 700mAh/ml level. Because of this restriction, it is necessary, for an improvement with standardized secondary batteries, to develop cathode material having a capacity of 700mAh-h/ml or more.

[0009] Here, as indicated in JP H7-240201A, proposals were made to appropriately use alloy material for cathode material. In that patent the appropriateness of non-ferrous metals comprised on transition elements, for example,  $\text{CoSi}_{2-3}$ ,  $\text{Mn}_2\text{Si}$ ,  $\text{Mo}_3\text{Si}$ ,  $\text{NiSi}$ , and  $\text{WSi}_2$  are indicated. In addition, in the 1995 investigative battery meeting, announcements were made concerning improvements in charging properties by  $\text{NiSi}_2$  intermetallic compounds in "Lithium Secondary Battery Properties for  $\text{ZnS-CaF}_2$  Type Constructed Intermetallic Compounds."

[0010] This paper discusses the use for cathode material of  $\text{NiSi}_2$  intermetallic compounds, however, there is no easy preparation of intermetallic compounds from industry metallurgical processes using molten  $\text{NiSi}_2$ . As is clear from the Ni-Co binary condition diagram, alpha  $\text{NiSi}_2$  intermetallic compounds exist at the locations containing 66.7 at% Si in Ni, and if the molten  $\text{NiSi}_2$  is cooled, at slightly higher temperatures than 1100 °C, Si separates out and grows.  $\text{NiSi}$  and  $\text{NiSi}_2$  result as the molten metal is cooled until the eutectic point. However, only a slight amount of the  $\text{NiSi}_2$  intermetallic



compound appears. In this way, because it is not possible to easily manufacture the intermetallic compound from the molten metal, the intermetallic compounds valuation for industry is low.

[0011] This invention has a goal of providing a lithium secondary battery containing metal silicide materials for the cathode materials which give the battery large charging capacity.

[0012] [Means for Solving the Problems]

This invention by using silicide materials with metals for the cathode material achieves the solution of conventional technology issues. That is, by having the silicides of Ni, Fe, Co, and Mn contain crystalline substances or amorphous substance in part, the discovery was made that a remarkable improvement in charging and discharging capacity was obtained. Furthermore, by separating out in part metals such as Sn and V, further improvement occurred. The cathode material relating to this invention is an intermetallic silicide as previously described, with composition of  $M_{100-x}Si_x$  ( $x \geq 50$  at%), M denoting at least one kind of element selected from Ni, Fe, Co, and MN. If the amount of the silicon exceeds 50at%, silicon crystallization easily separates out. In addition, if the amount exceeds 90at%, because manufacturing becomes indusssamplely difficult, a preferred range is 55-85at%.

[0013] Furthermore, improvements in charging capacity can be made by employing cathode material expressed by the general formula  $M_{100-x-y}B_ySi_x$  ( $x \geq 50$ at%,  $0 < y < 10$ at%) which had added additives to the

previously described cathode material. In this formula, along with M denoting at least one element selected from Ni, Fe, Co, MN, B denotes a silicide containing at least one kind selected from Sn, V, Cu, Ag, Al. The elements Sn, V, Cu, Ag, and Al expressed by B have the effect of increasing the charging capacity. The limit of this increase is 10at%. Especially, Sn and V improve the charging capacity more than other additives, with a desirable improvement in the range of 3-8at%. The elements expressed by B advance alloying of the silicon and lithium ions when charging and decomposition when discharging. Especially, Sn and V separate out between the dendrite shaped silicon crystals and the metal silicide material, having the effect of increasing the charging amount compared to other elements.

[0014] By finely crystallizing the metal silicide, and because it is possible to expand the surface area where lithium and silicon make contact, it is possible to promote chemical reactions very efficiently. Along with imparting an improvement in charging/discharging capacity, higher capacity is achieved. There are methods, such as quenching molten material that can be used to obtain fine silicon crystals. When making metal silicides, because there is sufficient time to grow crystals using a cooling process using general dissolution methods, the silicon crystals end up being large. However, with quenching molten materials, there can be obtained a mixture of fine crystals and amorphous materials under manufacturing conditions. It is not necessary that the entire product be fine

crystals, and there may be fine crystals if the effect of this invention is achieved.

[0015] Furthermore, by dendriting the silicon crystals, an effect is obtained which expands the contact surface area with the lithium, and it is possible to increase the charging/discharging capacity. When comparing cathodes made of carbon material, the conventional material, it is possible to obtain lithium secondary batteries with larger charging/discharging capacity even with batteries of the same size. Ni, Fe, Co, and Mn which are added to the silicon form amorphous alloys with the silicon, and at the same time there is a matrix which maintains fine dendritic silicon crystals, which are used as electrodes because the crystals receive silicon atoms and electrons. Below, an explanation is given in detail for concrete embodiments of this invention.

#### [0016] [Implementations]

First, an explanation is given below of the preparation method for trail materials. Make the prescribed stoichiometrically mole ratios of the composite metals and dissolve at high frequency in the atmosphere. Prepare a thin fragment for trail material of this molten material using a single roller (peripheral speed 30 m/s, teeming carried out on the copper roll, quenching at a rate of  $10^4\text{K/sec}$ ). For each kind of quenching method, the cooling rate using a method which supplies a water tank at a rate of  $10^2\text{K/sec}$ , whose rate is increased to  $10^{4-5}$  by atomizer methods which sprays the dissolved metal material

with nitrogen gas and water, but with the method which introduces into the water tank to obtain this invention's fine Si crystals, the silicon crystals grow, and the cooling rate is insufficient. Consequently, the atomize method and single roll method of cooling are appropriate and if the method can produce fine crystals, the effect of the invention obtained will be sufficient.

[0017] The thin fragments that are obtained by the single roll method are pulverized by a disc mill, passing through a sieve of 100 microns, passing through a fine powdering process by a jet mill, and after fixing the particles diameters, the material is used as cathode material. If the particle diameter is too large, it is not possible to produce a contact area with the silicon ions above a specified value, and in addition, considering the charging rate of the conductive binder used in the process of forming the cathode, the average diameter of the fine powder is desirable at 30 microns or less. However, if the particle diameter is too small, because the resistance of the electrode part, as a great deal of binder becomes necessary, the 10 micron level is appropriate. By mixing 12 wt.% graphite (KS-15) as a conductor for this fine powder, and in addition, 7 wt. % polyvinylidene-fluoride (PDVF), a conductive binder is made. The polyvinylidene-fluoride 7 wt. % was determined based on operating conditions under pressure bonding. A sample electrode was prepared by mixing the sample powder and conductive binder and pressure bonding (press pressure: 1t/cm<sup>2</sup>).

[0018] The charging/discharging sample device , as shown in Fig. 1 is formed from a device which can be charged and discharged by a constant current electrical source, an electrolyte tank, sample electrode, and reference electrode (lithium foil), anode (lithium foil). Because this charging/discharging experimental device is used for the experimentation for cathode properties, the anode 3 uses lithium, and while switching the experimental electrode 1, measurements were made of the charging/discharging properties. A 1 mol/liter solution was made of  $\text{LiPF}_6$  in an organic solution which had mixed 1:2 ethylene carbonate (EC) and methyl ethyl carbonate (MEC) in electrolyte solution 12. The switch 7 is moved to a charge position and the electric source 23 was charged so that the current density at the experimental electrode 1 was  $0.5\text{mA}/\text{cm}^2$ , and charging was done until the potential of the corresponding reference electrode 2 was lowered to 10mV. The switch 7 was switched for measurement of the discharging capacity, and discharging occurred until the potential of the experimental electrode 1 was raised to 0.8V with respect to the reference electrode. The discharge amount was calculated as the value which divided this quantity of electricity amount by the sample weight.

[0019] Following the previously described fabrication method, prepare as cathode material  $\text{M}_{100-x}\text{Si}_x$  (x: at %), and measure using this cathode the discharging capacity. The results are shown in Fig. 2 indicating a relationship between the silicon amount of the

intermetallic silicide and the discharging capacity. If the silicon is 50at% or more as shown in the figure, it is possible to quickly add discharging capacity and there is a tendency to saturate near 85 at%. By making the silicon at 50 at% or more, properties can be achieved which exceed 500mA-h/cc, and if at 70 at% or more, it is understood from Fig. 2 that it is possible to greatly improve the discharge capacity compared to conventional carbon.

[0020] Next, prepare cathode material which variously changes  $x$  and  $y$  using  $M_{100-x}Si_x$  and  $M_{100-x-y}B_ySi_x$ , and using the materials obtain the discharging capacity. Here, assume  $M = Ni$ , and for embodiments 1, 2, 3, 4, and 5, use the cathode materials whose composition is  $x = 56$  at%, 67, 71, 73, and 85, and with a comparative example 1 use  $x =$  at%. With embodiment 6 use Ni and Mn. As for including the additive element B, use for each embodiment 7-11, assume Cu, Sn, V, Ag, and Al as B in  $x = 71$ at %,  $y = 5$ at%  $Ni_{24}B_5Si_{71}$ . In addition, in order to compare with current materials, evaluate using the same method by fabricating the sample electrode 1 using carbon, thus creating comparative example 2. Comparative example 2 has the same composition as embodiment 2, but comparative example 3 was an alloy obtained by gradually cooling until normal temperature the molten materials from a temperature of 1400 °C. Table 1 shows these evaluation results.

[0021] [Table 1]

a	c	組成 (at比)	d	e	f
			放電容量 (mA-h/g)	比重 (g/ml)	放電容量 (mA-h/ml)
実施例 1		Ni <sub>44</sub> Si <sub>56</sub>	146	5	730
実施例 2		Ni <sub>33</sub> Si <sub>67</sub>	190	4.8	900
実施例 3		Ni <sub>28</sub> Si <sub>72</sub>	310	4.2	1300
実施例 4		Ni <sub>27</sub> Si <sub>73</sub>	440	4	1760
実施例 5		Ni <sub>15</sub> Si <sub>85</sub>	672	3.6	2420
実施例 6		Ni <sub>24</sub> Mn <sub>5</sub> Si <sub>71</sub>	291	3.6	1047
実施例 7		Ni <sub>20</sub> Cu <sub>5</sub> Si <sub>75</sub>	359	3.6	1290
実施例 8		Ni <sub>24</sub> Sn <sub>5</sub> Si <sub>71</sub>	550	3.6	1980
実施例 9		Ni <sub>21</sub> V <sub>6</sub> Si <sub>73</sub>	371	3.6	1335
実施例 10		Ni <sub>21</sub> Ag <sub>6</sub> Si <sub>73</sub>	228	3.6	820
実施例 11		Ni <sub>24</sub> Al <sub>5</sub> Si <sub>71</sub>	239	3.6	860
b					
比較例 1		Ni <sub>55</sub> Si <sub>45</sub>	10	6	60
比較例 2		カーボン	350	2.2	770
比較例 3		Ni <sub>33</sub> Si <sub>67</sub> 徐冷	25	5.0	125

Key: a) Embodiment; b) Comparative Example; c) Composition (at ratio); d) Discharging capacity; e) Specific gravity; f) Discharging capacity.

a	c	d	e	f
実施例	組成 (at比)	放電容量 (mA-h/g)	比重 (g/ml)	放電容量 (mA-h/ml)
実施例 1	Ni <sub>44</sub> Si <sub>56</sub>	146	5	730
実施例 2	Ni <sub>33</sub> Si <sub>67</sub>	190	4.8	900
実施例 3	Ni <sub>27</sub> Si <sub>73</sub>	310	4.2	1300
実施例 4	Ni <sub>27</sub> Si <sub>73</sub>	440	4	1760
実施例 5	Ni <sub>16</sub> Si <sub>84</sub>	672	3.6	2420
実施例 6	Ni <sub>14</sub> Mn <sub>6</sub> Si <sub>80</sub>	291	3.6	1047
実施例 7	Ni <sub>14</sub> Cu <sub>6</sub> Si <sub>80</sub>	359	3.6	1290
実施例 8	Ni <sub>12</sub> Sn <sub>2</sub> Si <sub>86</sub>	550	3.6	1980
実施例 9	Ni <sub>14</sub> V <sub>6</sub> Si <sub>80</sub>	371	3.6	1335
実施例 10	Ni <sub>14</sub> Ag <sub>6</sub> Si <sub>80</sub>	228	3.6	820
実施例 11	Ni <sub>14</sub> Al <sub>6</sub> Si <sub>80</sub>	239	3.6	860
b 比較例 1	Ni <sub>55</sub> Si <sub>45</sub>	10	6	60
比較例 2	カーボン	350	2.2	770
比較例 3	Ni <sub>12</sub> Si <sub>88</sub> 徐冷 <sup>g</sup>	25	5.0	125

Key: a) Embodiment; b) Comparative Example; c) Composition (at ratio); d) Discharging capacity; e) Specific gravity; f) Discharging capacity; g) gradual cooling.

[0022] As is understood from Table 1, the embodiments with Ni(Mn)<sub>100-x</sub>Si<sub>x</sub> and Ni<sub>100-x-y</sub>B<sub>y</sub>Si<sub>x</sub> have extremely large discharging capacities compared to any conventional material (comparative examples). Using Ni<sub>100-x</sub>Si<sub>x</sub>, x becomes in excess of 50, and following the increase, the discharging capacity increases. The addition of Sn and V as additive elements B have a larger discharge capacity compared with those examples which did not have additives.

[0023] As indicated Comparative example 3 had the same fabrication as Embodiment 2, and obtained an alloy by gradually cooling to normal temperatures the molten material from 1400 °C. The



measurements of the discharge capacity with this alloy as the cathode material only indicated an extremely small discharge capacity when compared with that of the invention at 125mAh/ml. Fig. 3 shows the X-ray diffraction pattern of this embodiment 2 alloy, Fig. 4 shows an electron microscope microstructure photo seen at 50 times magnification of this alloy, Fig. 5 shows the X-ray diffraction pattern of the Comparative example 3, and Fig. 6 shows the electron microscope microstructure photo seen at 50 times magnification of the alloy. Only the silicon peak is clear from embodiment 2, but from Embodiment 3, the silicon peak and the NiSi peak is visible. The silicon peak in comparative example 3 appears very clear, and corresponds to the large silicon crystals separating out as in the electron microscope photo (reference Fig. 6). The separation of the fine silicon crystals as in embodiment 2 indicates a large discharge capacity.

[0024] Next, in order to see Sn's additive effect, the discharge capacity was obtained after adding to 10 at% Sn based on the composition  $\text{Ni}_{29}\text{Si}_{71}$  in Table 1's Embodiment 3. Fig. 7 shows these results. As is clear from the results, with Sn in the range of 3-8 at%, a large improvement occurs compared to when no Sn is added. Especially, a maximum value is indicated in the neighborhood of 5at%. In addition, the same effect is realized with V.

[0025] Fig. 8 is an electron microscope photo of Embodiment 8. With this electron microscope photo, a small white point between the

dendritic silicon crystals is the separation of Sn, and shows a nearly uniform distribution for the metal silicide material. Along with the existing fine dendritic silicon crystals, a lithium battery of extremely large capacity is obtained when using an alloy for which Sn separates as cathode material. The fine dendritic silicon crystal makes lithium ions and the alloy, and conversely, lithium ion absorption and discharge is promoted. When using the electron microscope, it is understood that the proportion which occupies the fine dendritic silicon crystals generated by embodiment processes having large capacity and by the rapid cooling process is large.

[0026] In the embodiments, all M can be used for Ni, and as shown in embodiment 6, one part may be replaced by Mn. In addition, in place of Ni, it is possible to use by combining one kind of Mn or a combination.

[0027] [Effect of the Invention]

According to this invention, compared to carbon which is used conventionally for cathodes, in addition to being able to greatly improve the charging and discharging capacities, it is possible to improve safety and reliability in order to use silicides formed between metals which are not flammable.

[Explanation of the Elements]

[Fig.1] A outline construction diagram of the charging and discharging device.

[Fig. 2] A graph which shows the charging and discharging properties when changing the Si amount using cathode material which is used in this invention.

[Fig. 3] A X-ray diffraction diagram of embodiment 2's cathode material (quenched  $\text{Ni}_{33}\text{Si}_{67}$  alloy) used in this invention.

[Fig. 4] An electron microscope photo of embodiment 2's cathode material (quenched  $\text{Ni}_{33}\text{Si}_{67}$  alloy) which is used in this invention).

[Fig. 5] An X-ray diffraction diagram of the cathode material (gradually cooled  $\text{Ni}_{33}\text{Si}_{67}$  alloy) of comparative example 3.

[Fig. 6] An electron microscope photo of the cathode material (gradually cooled  $\text{Ni}_{33}\text{Si}_{67}$  alloy) of comparative example 3.

[Fig. 7] A graph which shows the discharging properties when increasing the additive amount of Sn in cathode material which is used in this invention.

[Fig. 8] An electron microscope photo of the cathode material ( ) of embodiment 8 used in this invention.

[Explanation of the Elements]

1- sample electrode, 2- reference electrode (Li), 3- anode, 11, tank, 12- electrolyte solution, 21- electrical source, 22- amp meter used for discharging, 23- electrical source, 24- amp meter for charging, 25- voltage meter

Figure 1

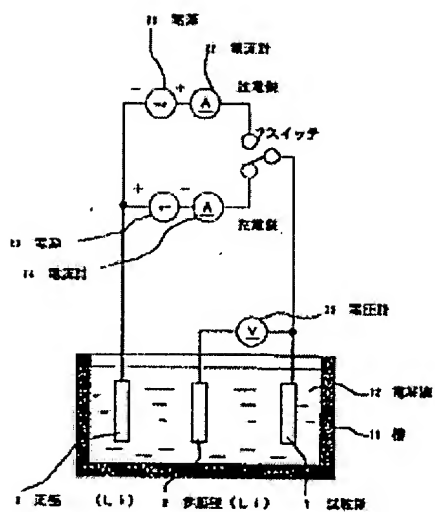
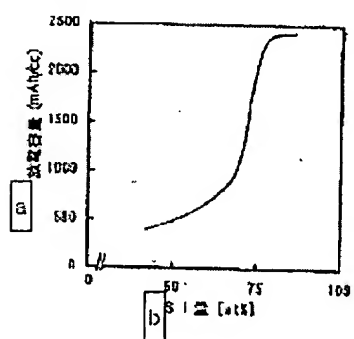
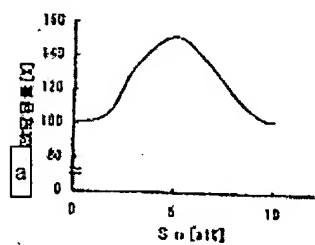


Figure 2



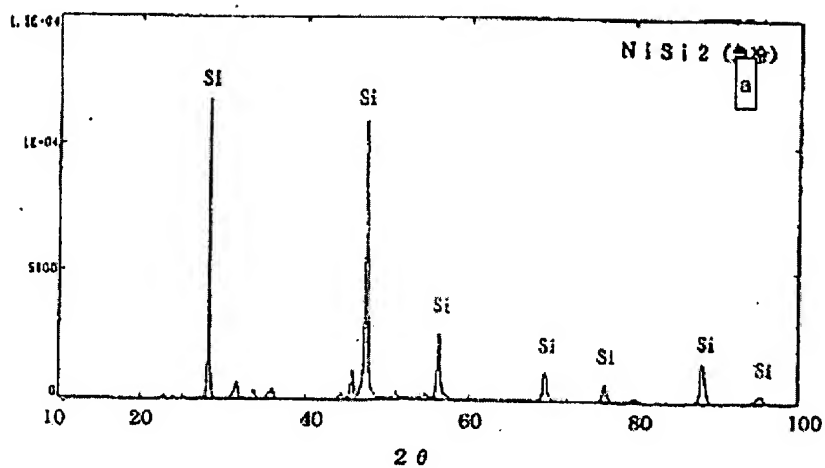
Key: a) Discharge capacity; b) Si amount.

Figure 7



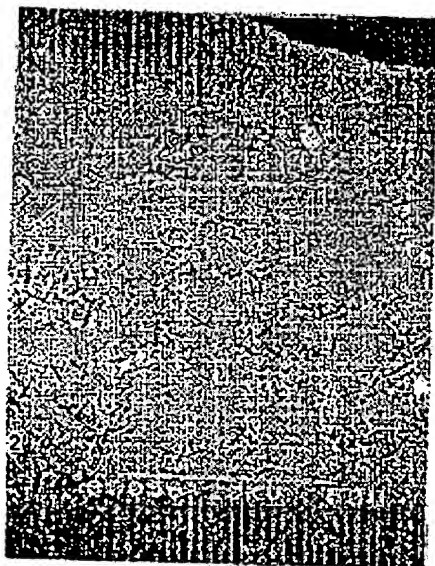
Key: a) Discharge capacity.

Figure 3

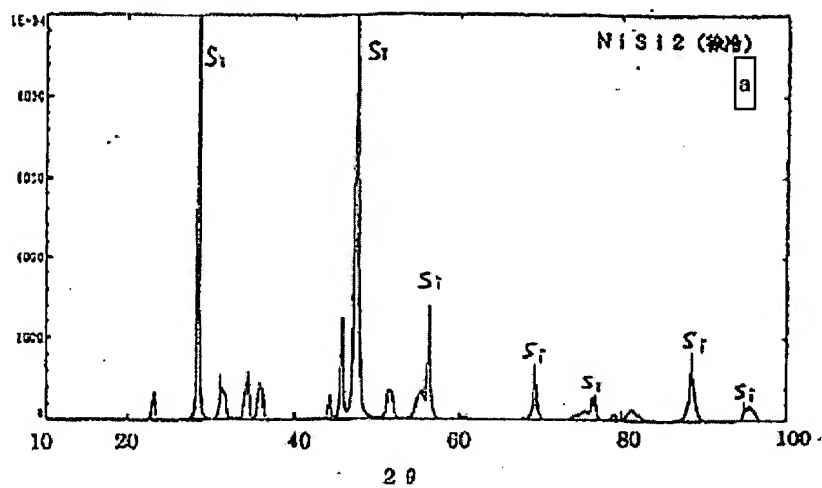


Key: a) Quenching.

Figure 4. Photo substituting for diagram



/9



Key: a) Gradual cooling.

Figure 8. Photo substituting for diagram

